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PROCESSING OF STRONG FLUX TRAPPING HIGH T_c OXIDE SUPERCONDUCTORS

Center Director's Discretionary Fund Final Report

By M. K. Wu, C. A. Higgins, P. T. Leong, H. Chou, B. H. Loo, P. A. Curreri, P. N. Peters, R. C. Sisk, C. Y. Huang, and Y. Shapira

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INTRODUCTION

The discovery of high temperature superconductivity in copper oxide [1-4] has generated activities at an unprecedented level in laboratories around the world in the past year or so. Recently, superconducting transition temperature T_c has been raised to about 120 K in Tl-Ba-Ca-Cu-O compounds [4]. Although there have been numerous efforts to characterize the high T_c oxide compounds, the mechanism responsible for the observed high T_c has not been fully understood. Furthermore, the technological feasibility of the high T_c oxide superconductors has yet to be demonstrated. The most serious problems preventing the use of these materials, especially in bulk applications, are the low current densities and the lack of usable shapes with sound mechanical integrity.

About a year ago, the possibility of raising the critical current density in the bulk oxide superconducting material by dispersing fine metal through a dispersion of fine metal oxide was explored. As a result of these studies, a novel effect, in which a cooled superconductor can be suspended in a space below a permanent magnet [5], was discovered. This suspension effect differs significantly from the more familiar levitation effect, which usually shows a small permanent magnet floating above a superconducting pellet cooled in liquid nitrogen. In the suspension effect, a strong permanent magnet was lowered toward the superconducting disc until the distance was no more than a few millimeters. Then the magnet was raised, and the superconductor was attracted toward it and remained suspended at some distance. This suspension effect may have important applications, such as in the handling of radioactive wastes and hazardous materials, and in frictionless bearings.

This suspension effect was first observed in samples of $YBa_2Cu_3O_7$/AgO (Y-123/AgO) composites [5]. Magnetization measurements [6] of these samples show a much larger hysteresis, which corresponds to a large critical current density interpreted within the Bean critical state model [7]. These data also provide a quantitative explanation of the magnetic suspension [6]. Furthermore, the electrical resistivity measurement in magnetic field shows that the critical field is about three times larger than that of the Y-123 bulk material.

In addition to the Y-123/AgO composite, a similar suspension effect in other RE-123/AgO composites, where RE stands for rare-Earth elements, has also been observed. Some of these composites exhibited even stronger flux pinning than that of Y-123/AgO composite. In addition, flux pinning properties of these composites depend critically on the sintering temperature. This paper presents detailed processing conditions for these RE-123/AgO composites, as well as magnetization and critical field data of these composites.

EXPERIMENTAL

The starting superconducting RE-123 compounds were prepared in the following manner. Appropriate amounts of metal oxides were mixed, pressed into pellets, heated at 950°C for 12 hr, and then quenched to room temperature. Reacted pellets were reground, pressed, and annealed in oxygen flow at 950°C for 6 hr, and then furnace cooled. These high quality single phase RE-123 compounds were then mixed with AgO with a weight ratio from 1:1 to 7:1. The well-mixed powders were pressed into pellets and then annealed. Annealing temperatures are detailed below. Electrical resistivity measurements were made with the conventional four-probe technique. The dc magnetic moment measurements were made with a quantum design MPMS SQUID magnetometer. High field measurements were performed at Francis Bitter National Magnetic Laboratory at the Massachusetts Institute of Technology (MIT). A standard four-probe using pulse current was used to determine critical current density at zero field. Structural and phase determinations were made by x-ray diffraction and Raman microprobe analyses.

RESULTS AND DISCUSSION

The optimal heat treatment conditions for the formation of strong flux pinning RE-123/AgO composites are listed in Table 1. The specific weight ratio of RE-123 to AgO is 3:1. The data show that sintering temperatures are different for different RE-123 compounds. In general, the temperatures required are higher than the temperatures needed to form the corresponding RE-123 compounds, and they do not depend on the weight ratio of RE-123 to AgO. The sintering time used was 12 hr, although the effect of sintering time has yet to be determined. It is interestinng to note that the sintering temperature depends on the ionic size of the rare-Earth element. The empirical trend is that a larger rare-Earth ion requires higher sintering temperatures. It was also found that flux pinning materials of RE-123/AgO composites form only a narrow sintering temperature range.

The strong flux pinning effect observed in these RE-123/AgO composites may be due to the interdiffusion of the silver metal, which was formed from the dissociation of AgO at above 220°C, to the superconducting grains or grain boundaries. It may also be due to the Ag-promoted mechanical integrity through dispersion strengthening or cohesive effects at particle boundaries and grain boundaries of the RE-123 materials. The sensitivity of the observed pinning effect to the sintering temperature may be due to the change of the interdiffusion rate of silver metal with the superconducting particles, particle surfaces, and particle grain boundaries. If interdiffusion of Ag is critical, then AgO particle size and RE-123 grain size will be important variables, as well as the reaction temperature and time. Preliminary results show that finer starting material particles give stronger pinning effect.

Typical temperature dependence of the resistance of RE-123/AgO composites is illustrated in Figure 1. The behavior is very similar to that of the corresponding RE-123 compound except that its overall resistance is lower. Exceptions are the Eu-123/AgO and Gd-123/AgO composites. The superconducting transition temperature T_c of the composite remains almost unchanged compared

with that of the starting RE-123 compounds. The decrease in the normal state resistivity with the addition of silver oxide suggests a lowering of contact resistances between grains. Near identical T_c's suggest that grain interiors experienced little change from the starting RE-123 compounds. One important advantage derived from these RE-123/AgO composites is the reduction of overall contact resistance. For instance, direct determination of J_c using four-point I-V measurements can be performed without any contact problem in these RE-123/AgO composites. Results of these measurements will be published later.

The resistance of the Y-123/AgO (3:1) composite near T_c as a function of magnetic field in a Bitter magnet has also been measured. The result is displayed in Figure 2. It is clear that at 85 K the resistance is zero in a field of 10 T. It should be pointed out that with the experimental error, the resistance is still zero below 80 K for $H < 20$ T (not shown). This is in strong contrast with a typical sintered RE-123 bulk material in which the resistance at 77 K is about one-half the normal resistance above T_c. This result suggests that the upper critical field H_{c2} in the Y-123/AgO is much higher. If the midpoint of the transition is taken, $(dH_{c2}/dT)_{T_c} = -3.2$ T/K. Using WHH theory [8], it is found that $H_{c2} = 0.69\ T_c(dH_{c2}/dT)_{T_c} = 200$ T. It is believed that even larger H_{c2} values can be achieved in these RE-123/AgO composites when optimal conditions in terms of the relative particle or grain sizes of the superconducting and AgO powders are achieved.

The magnetic magnetization of these RE-123/AgO composites at 77 K is also compiled in Table 1. The values are generally comparable with those of the corresponding RE-123. Figure 3 shows the temperature dependence of magnetic moment of Eu-123/AgO composite. The value of 130 emu/g for Eu-123/AgO composite at 4.2 K was the largest among all the polycrystalline high temperature oxide superconductors. The M-H hysteresis loop for Y-123/AgO measured at 77 K to a maximum field $H_{max} \pm 0.6$ kOe is shown in Figure 4. It was taken after the sample was cooled in zero field, and was independent of the sweep rate between 0.03 and 0.4 kOe/min. The critical current density estimated from the magnetization at 0.1 kOe is 3.3×10^3 A/cm^2, based on Bean's critical state model [9]. This value of J_c is an order of magnitude larger than that measured from transport properties. The residual magnetization is 3 emu/g, and is not sensitive to the maximum field larger than 0.5 kOe.

The possible origin of flux pinning may be that the cell has a normal metal boundary or precipitate in it, resulting in a Josephson-type boundary. The enhancement in magnetic and electric properties, and the suspension effect of the RE-123/AgO composites, can be modeled in terms of the existence of many weak-link current loops, where the weak links are associated with the inter-grain contacts. When a sample is brought into the gradient field of a magnet, the increasing field induces diamagnetic currents in all loops. When a critical current is exceeded in some loop, flux enters that loop, the current drops momentarily, and the flux is trapped. Bringing the sample closer to the magnet results in additional flux trapping in weaker loops and further diamagnetic current growth in stronger loops. The induced diamagnetic currents generate repulsive forces in the gradient field. If at any point in this process the sample moves away from the magnet, changes in currents and field would reverse. Loops with no trapped flux continue to cause repulsion, which is decreasing. However, the currents in the loops with trapped flux will decrease and eventually reverse direction, attempting to prevent flux flow out of the loops. This generates an attractive force in the gradient field. Silver oxide mixing enhances the critical currents of inter-grain contacts, thus providing stronger pinning forces.

High values of the critical current density usually result from strong interactions that prevent the motion of flux lines. The metallurgical problems are similar to those of producing mechanically strong or magnetically hard materials. In mechanically strong materials, the movement of crystal dislocations is hindered by regions whose elastic properties differ from those of the bulk of the material. It is expected that in high current superconductors, regions whose superconducting properties show a difference from those of the bulk of the material will interfere with the motion of flux lines. The greater the difference, the stronger the pinning. The region may be more strongly superconducting than the bulk (i.e., have higher T_c and H_c), be less superconducting, and be nonsuperconducting. The nature and origin of these regions in general are imperfections of the crystal. Such regions are most effectively produced by precipitation, powder metallurgy, and dislocation cell structure. For a given volume fraction of these regions, the more finely divided the structure, the stronger the pinning. Other factors such as the crystal anisotropy, oxygen stoichiometry, and microcracks are also important in determining the critical current density. The exact reason for the observed current density enhancement in RE-123/AgO composites has yet to be determined. More detailed study on the correlation between microstructure and sintering conditions of these materials is needed to better understand the mechanism responsible for the strong pinning effect.

CONCLUSIONS

The studies presented here indicate that proper processing conditions are critical for the formation of strong flux pinning RE-123/AgO composites. Two orders of magnitude enhancement in critical current density relative to the starting RE-123 compounds were observed in these composites. Materials prepared with finer particle sizes resulted in much stronger pinning. Resistive measurement in field shows that the upper critical field in Y-123/AgO is about three times larger than that of the Y-123 compound.

REFERENCES

1. Bednorz, J. G. and Muller, K. A.: Z. Phys., Vol. B64, 1986, p. 189.

2. Wu, M. K., Ashburn, J. R., Torng, C. J., Hor, P. H., Meng, R. L., Gao, L., Huang, Z. J., Wang, Y. Q., and Chu, C. W.: Phys. Rev. Lett., Vol. 58, 1987, p. 908.

3. Maeda, H., Tanaka, Y., Fukutomi, M., and Asano, T.: Jpn. J. Appl. Phys. Lett., Vol. 27, 1988, p. L209.

4. Sheng, Z. Z., Hermann, A. M., El Ali, A., Almason, C., Estrada, J., Datta, T., and Matson, R. J.: Phys. Rev. Lett., Vol. 60, 1988, p. 937.

5. Peters, P. N., Sisk, R. C., Urban, E. W., Huang, C. Y., and Wu, M. K.: Appl. Phys. Lett., Vol. 52(24), 1988, p. 2066.

6. Huang, C. Y., Shapira, Y., McNiff, J. J. Jr., Peters, P. N., Schwartz, B. B., Wu, M. K., Shull, R. D., and Chiang, C. K.: Modern Phys. Lett., in press 1988.

7. Bean, C. P.: Phys. Rev. Lett., Vol. 8, 1962, p. 250.

8. Werthanmer, N. R., Helfand, E., and Hohenberg, P. C.: Phys. Rev., Vol. 147, 1966, p. 295.

9. Muller, A.: Z. Naturforsch., Vol. 25A, 1970, p. 1659.

TABLE 1. RE-123 OXIDE SUPERCONDUCTORS AND RE-123/AgO COMPOSITES

Sample	Ann. Temp. (°C)	T_c(K)	R(250 K) (-cm)[a]	M(77 K) (emu/g)[b]
Nd-123/AgO	1030	90	423	-0.2037
Nd-123	1030	89	520	-0.2087
SM-123/AgO	1035	91	187	-0.3326
SM-123	960	96	486	-0.3634
Eu-123/AgO	1025	96	530	-0.2781
Eu-123	950	96	526	-0.0304
Gd-123/AgO	1020	93	1125	-0.0417
Gd-123	950	96	445	-0.0138
Dy-123/AgO	965	95	52	-0.3652
Dy-123	955	92	516	-0.1253
Ho-123/AgO	960	95	39	-0.3877
Ho-123	950	91	413	-0.3877
Er-123/AgO	960	91	165	-0.0366
Er-123	955	92	3205	-0.0032
Y-123/AgO	990	93	252	-0.0146
Y-123	950	94	803	-0.0131

a. Measured at zero field
b. Measured at 20 G

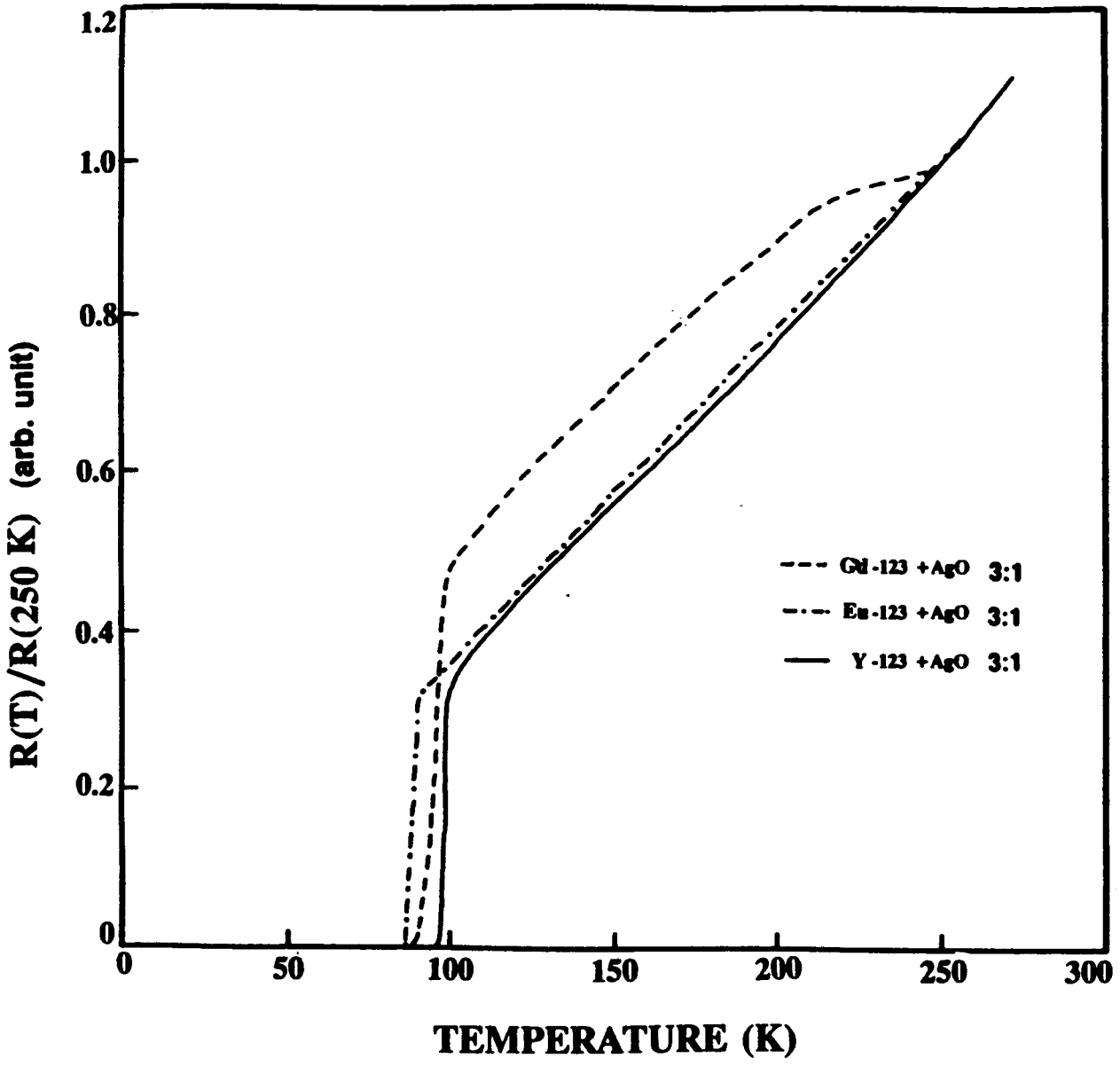

Figure 1. Temperature dependence of resistance of RE-123/AgO composites, where RE = Y, Eu, and Gd.

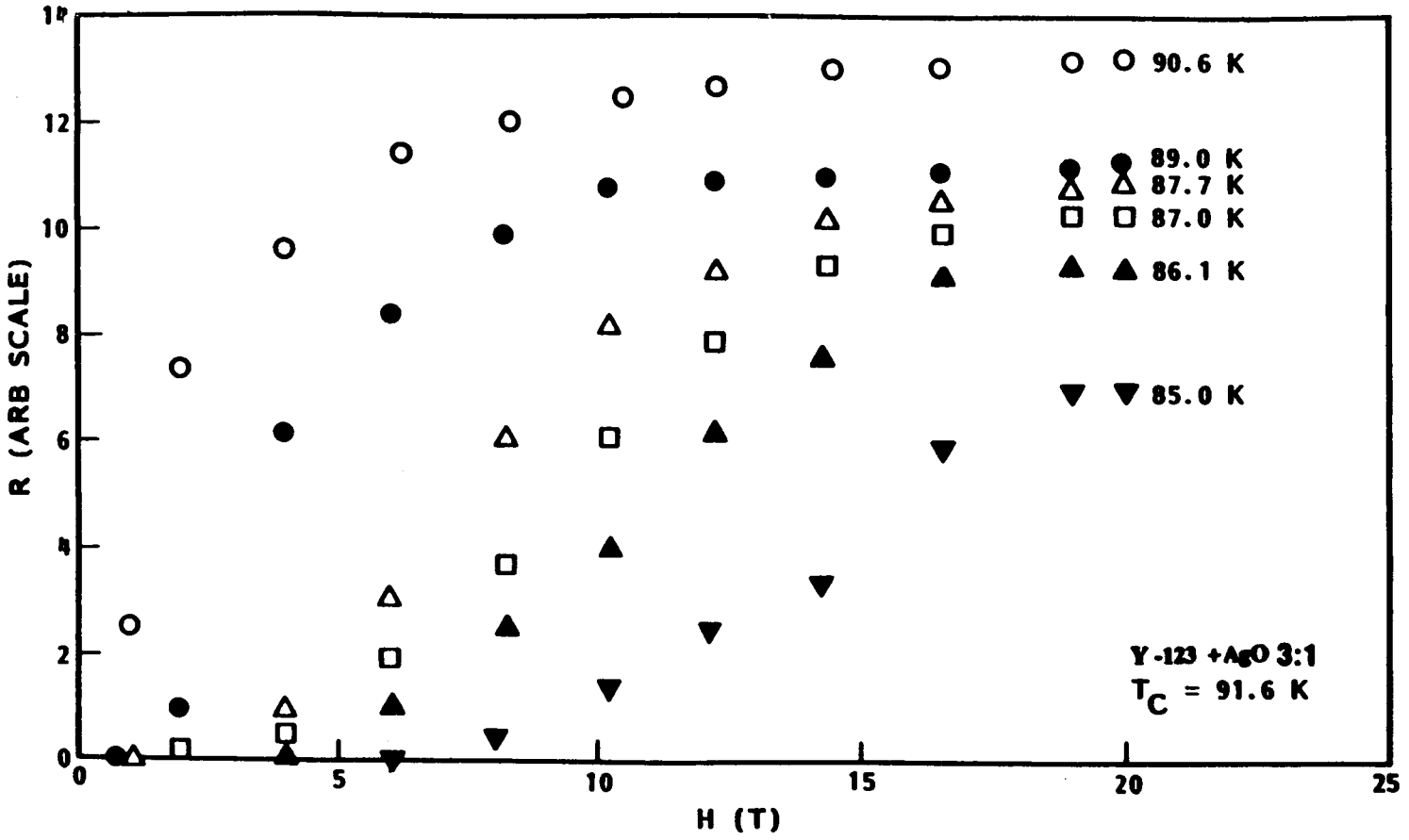

Figure 2. Field dependence of resistance of Y-123/AgO (3:1) composite at different temperatures.

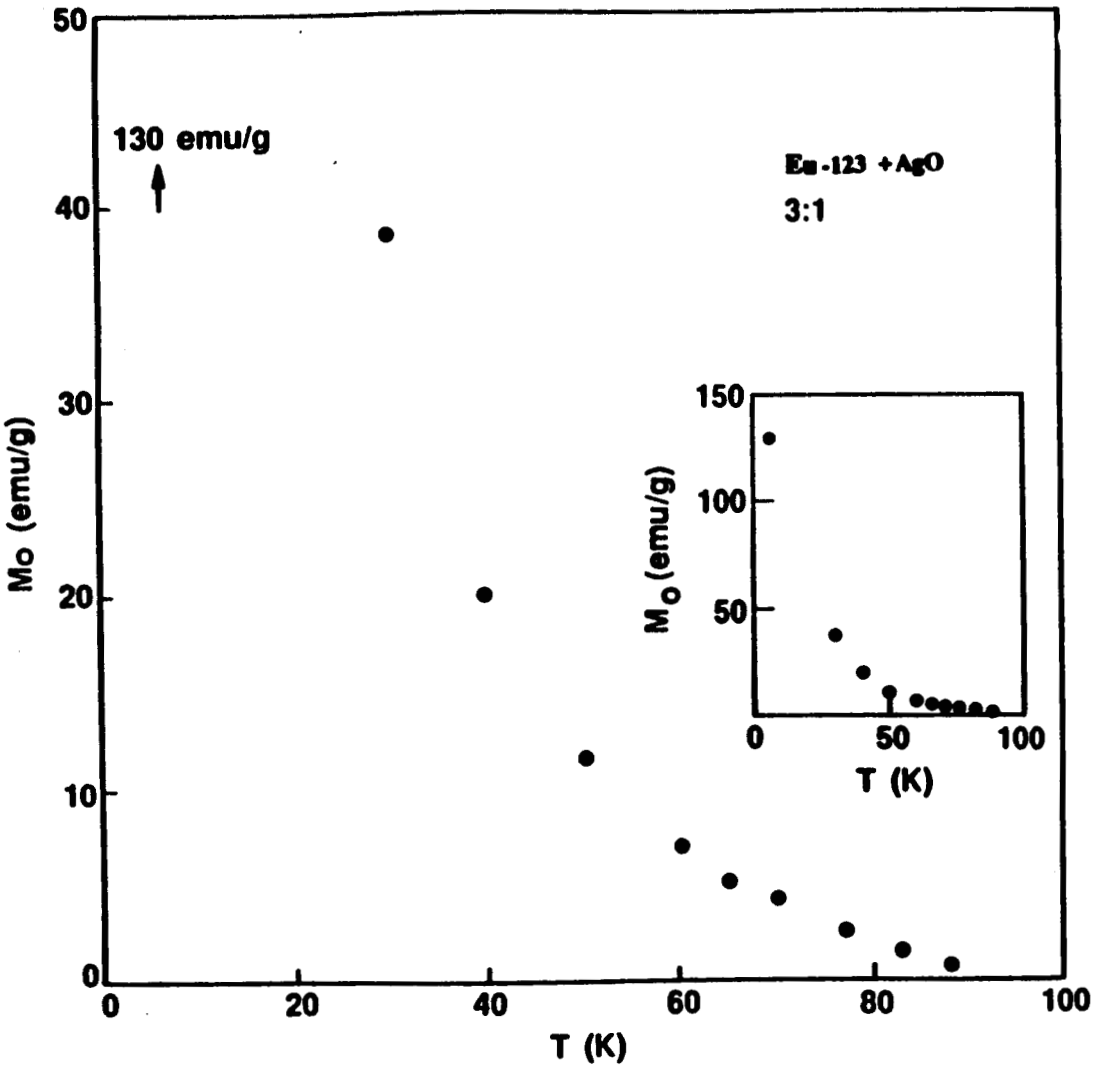

Figure 3. Magnetic moment of Eu-123/AgO (3:1) as a function of temperature.

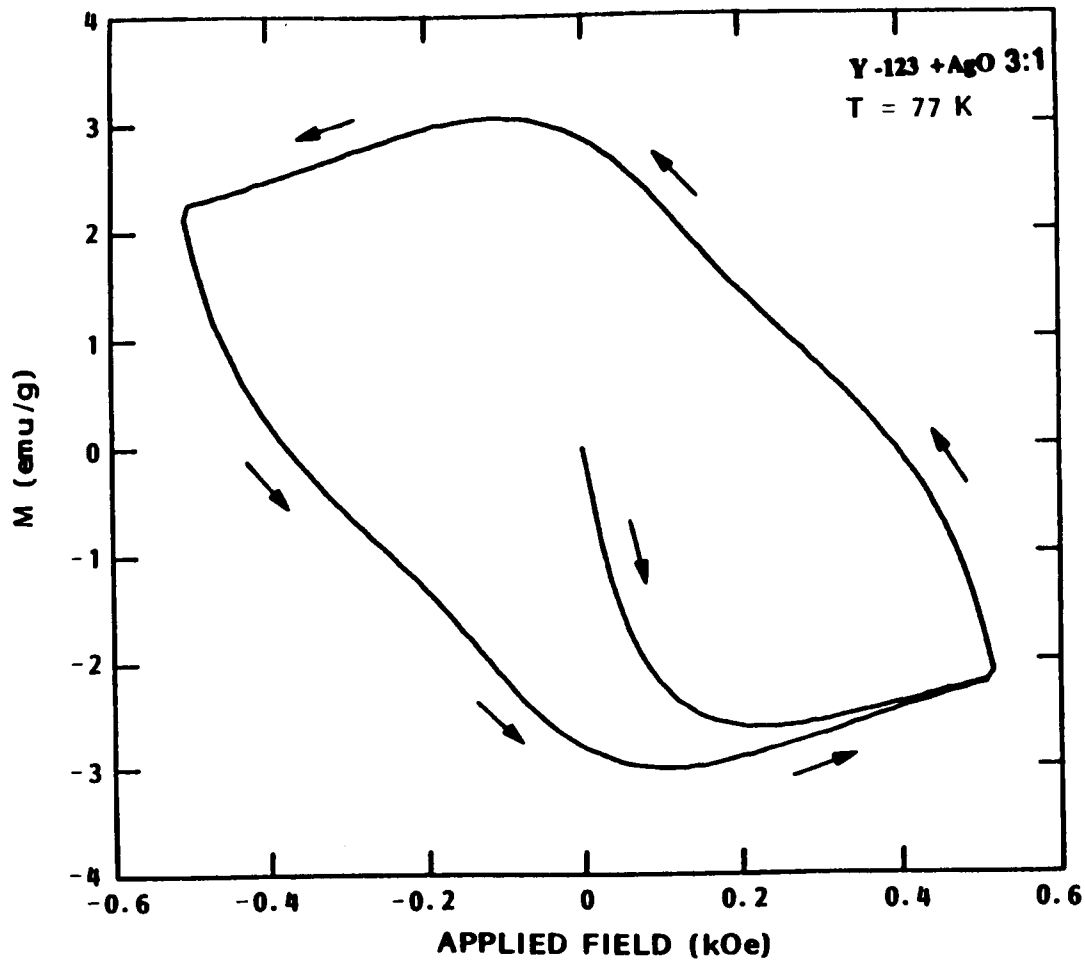

Figure 4. M-H hysteresis loop for Y-123/AgO composite at 77 K with H_{max} = 0.9 kOe. The trace was obtained after cooling in zero field.

APPROVAL

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

E. Tandberg-Hanssen

E. TANDBERG-HANSSEN
Director, Space Science Laboratory

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16. ABSTRACT

Magnetic suspension effect was first observed in samples of $YBa_2Cu_3O_7$/AgO (Y-123/AgO) composites. Magnetization measurements of these samples show a much larger hysteresis which corresponds to a large critical current density. In addition to the Y-123/AgO composites, recently similar suspension effects in other RE-123/AgO, where RE stands for rare-Earth elements, were also observed. Some samples exhibit even stronger flux pinning than that of the Y-123/AgO sample. An interesting observation was that in order to form the composite which exhibits strong flux trapping effect the sintering temperature depends on the particular RE-123 compound used. This paper presents the detailed processing conditions for the formation of these RE-123/AgO composites, as well as the magnetization and critical field data.

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